

A Novel Hydrogen Peroxide Sensor Based on Multiwalled Carbon Nanotubes/Poly(pyrocatechol violet)-Modified Glassy Carbon Electrode

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ABSTRACT: In this work, a new hydrogen peroxide (H_2O_2) sensor was reported based on electropolymerizing pyrocatechol violet (PCV) on a glassy carbon electrode modified with multiwalled carbon nanotubes (MWCNTs). The modified electrode was characterized by cyclic voltammetry (CV) and scanning electron microscopy. The result of electrochemical experiments showed a favorable catalytic activity toward the reduction of H_2O_2 at -0.4 V with a linear response range from 2.0 μM to 2.4 mM and a

detection limit of 0.7 μM (at a $S/N = 3$). The well catalytic activity of proposed sensor could be attributed to the poly-PCV/MWCNTs composite film on the electrocatalytic reduction of H_2O_2 . In addition, the sensor also exhibited a high sensitivity, good stability, and reproducibility. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3488–3493, 2009

Key words: H_2O_2 ; pyrocatechol violet; multiwalled carbon nanotubes; modified electrode

INTRODUCTION

Since the discovery of the carbon nanotubes (CNTs) in 1991,¹ they have been considered one of the most promising materials for field emission application, nanoscale electronic, and optoelectronic devices because of their high electrical conductivity, high aspect ratio "whisker-like" shape for optimum geometrical field enhancement and remarkable thermal stability. In recent years, the CNTs have been applied in various fields such as energy storage,² actuators,³ and sensors.⁴ Especially, it opens a new door for electroanalytical chemistry field because of its large specific surface area and good capability of electron transfer. It has been reported that CNTs modified electrodes were successfully applied to study and determine many biological and organic molecules such as ascorbic acid and uric acid,⁵ NADH,⁶ amino acids,⁷ rutin,^{8,9} hydrazine,¹⁰ H_2O_2 ,¹¹ adenine, and guanine.^{12,13}

In recent years, conducting polymer/CNTs-modified electrode has been of great interest in the electrocatalysis reactions because of their unique

chemical and electrochemical properties. It has also been demonstrated that the incorporation of CNTs into conducting polymer-modified electrode possess the properties of the individual components with a synergistic effect that would be useful in particular application.^{14–21} Among the various conducting polymers, organic dyes as particular conducting polymer monomer with a high application potential have become the most attractive one because of its facile preparation, high conductivity, and good environmental. A series of organic dyes such as neutral red,^{9,22–24} toluidine blue O,²⁵ alizarin red S,²⁶ congo red,^{27,28} and thionine^{13,29–31} have been used to prepare electrochemical sensors with CNTs, and they all exhibit excellent electrocatalytic ability to biological molecules.

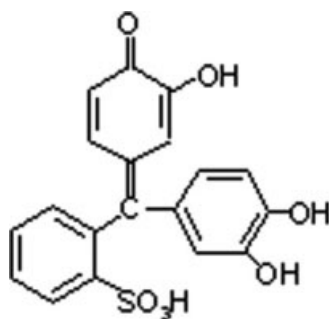
Pyrocatechol violet (PCV, with the chemical structure shown in Scheme 1), a dye in the triphenylmethane series, has been used for the determination of Al^{3+} ^{32,33} and other metal ions.³⁴ The monomer dyes possess very good electrocatalytic activity toward the redox of small molecular compounds such as ascorbic acid and dopamine,³⁵ hydrazine,³⁶ and NADH,³⁷ displaying excellent electron transform efficiency as an electron transfer mediator. Recently, Zheng and coworkers³⁸ reported H_2O_2 determination using carbon ceramic electrodes modified with PCV.

Over the last decades, the accurate determination of H_2O_2 has received considerable attention because it is an essential mediator in food, pharmaceutical, clinical, and environmental analysis. Enzyme (e.g.,

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Scheme 1 The structure of pyrocatechol violet (PCV).

peroxidase) electrodes have been fabricated for H₂O₂ detection with simplicity, high sensitivity, and selectivity,^{39,40} but their operational conditions are generally limited because of the denaturation of enzymes. Prussian blue (PB) and silver-DNA hybrid films have been developed as catalytic sensors to detect H₂O₂.^{41–46} Despite these advances, it is still a great challenge to construct highly selective, sensitive, stability, and biorecognition interfaces for the determination of H₂O₂.

In this article, the PCV was voltammetrically electropolymerized onto the glassy carbon electrode (GCE) modified with multiwalled carbon nanotubes (MWCNTs), and the resulting modified electrode was used to detect H₂O₂. The experimental results showed the proposed electrode exhibited a noticeable electrocatalytic property toward the reduction of H₂O₂ with a linear response range from 2.0 μ M to 2.4 mM, and the detection limit is 0.7 μ M. To our knowledge, this is the first application of poly-PCV/MWCNTs to fabricate an electrochemical H₂O₂ biosensor with a favorable performance for the rapid detection of H₂O₂.

EXPERIMENTAL

Apparatus and reagents

Electrochemical experiments were performed with a CHI 660B electrochemical workstation (CH Instruments, Chenhua Corp. Shanghai, China) with a three-electrode configuration. The bare or modified GCE (3.0 mm in diameter) was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. All the potentials quoted in this article were referred to the SCE.

MWCNTs (95% purity) were purchased from Chengdu Institute of Organic Chemistry of Academy of Sciences and synthesized by chemical vapor deposition. PCV was obtained from the Jiangsu Chemical Company (China). H₂O₂ and other chemicals were of analytical grade and were obtained from Shanghai Chemical Reagent (Shanghai, China) used without further purification. Voltammetric experiments

were carried out in solutions deaerated by pure nitrogen. The phosphate buffer solution (PBS, 0.1M) was prepared by 0.1M KH₂PO₄ and 0.1M K₂HPO₄, and then adjusted the pH with 0.1M H₃PO₄ and 0.1M KOH solutions. All the solutions were prepared with doubly distilled water, and all experiments were conducted at the room temperature.

Fabrication of the modified electrode

Prior to the modification, the bare GCE was polished successively with emery paper and alumina slurries (0.3 and 0.05 μ m), thoroughly rinsed with water and sonicated in nitric acid (1 : 1), acetone and doubly distilled water (each for 5 min). MWCNTs (1.0 mg) were dispersed in 10 mL *N,N*-dimethylformamide by ultrasonic agitation for about 60 min to get a 0.1 mg/mL black suspension. The MWCNTs-modified electrode was prepared by casting 5 μ L of the MWCNTs on a clean GCE surface, which was allowed to dry in air at room temperature, and then rinsed with doubly distilled water to remove the physical adsorption of MWCNTs. The obtained electrode was described as MWCNTs/GCE. The poly-PCV/MWCNTs-modified electrode was prepared by immersing the MWCNTs/GCE into 0.1M KCl solution containing 1.0 mM PCV by cyclic potential scan between +0.1 and +0.9 V at 20 mV/s for 16 cycles and rinsed with doubly distilled water.

RESULTS AND DISCUSSION

Electropolymerization of the PCV on MWCNTs/GCE

The electropolymerization process of PCV on MWCNTs-modified electrode was investigated by cyclic voltammetry (CV), which is shown in Figure 1.

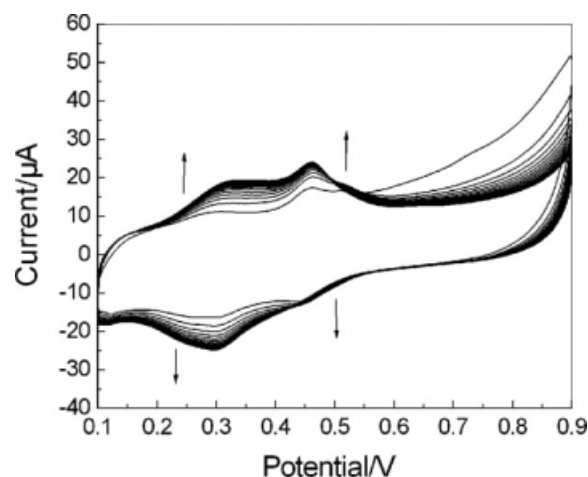


Figure 1 CVs of the poly-PCV film on a GCE modified with MWCNTs in 0.1M KCl solution containing 1.0 mM PCV. Scan rate: 20 mV/s.

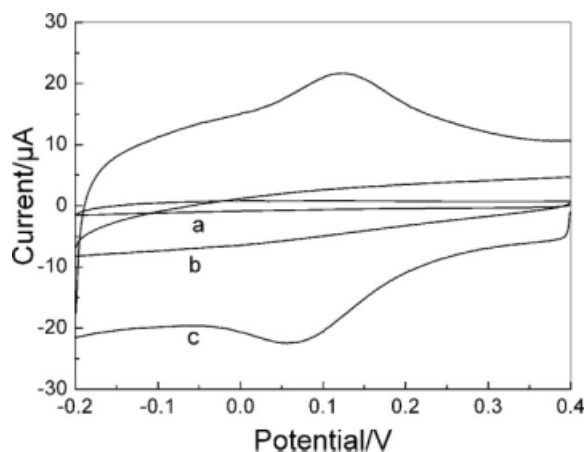


Figure 2 CVs of different electrodes in 0.1M PBS (pH 6.0): (a) bare GCE; (b) MWCNTs/GCE; and (c) poly-PCV/MWCNTs/GCE. Scan rate: 100 mV/s.

The CVs show that the currents of two pairs of reversible redox peaks increase gradually with increasing scan cycles. After CV scanning 16 cycles in the potential range from +0.1 to +0.9 V at 20 mV/s, the peak currents tended to become stable. This means that the PCV can be successfully electropolymerized and form conducting polymer on the surface of MWCNTs-modified electrode.

In this work, the modified electrode was characterized using electrochemical and microscopic methods [CVs and scanning electron micrograph (SEM)]. Figure 2 compared the CVs responses of the bare GCE, the MWCNTs/GCE, and the poly-PCV/MWCNTs/GCE in 0.1M PBS (pH 6.0). It was observed that no redox peaks appeared at GCE (a) and MWCNTs/GCE (b). However, for curve c, one pair of the obvious redox peaks was observed. According to the literature,³⁸ we suggested the obvious redox peaks were corresponding to one pair of the redox of poly-PCV on the surface of the modified electrode, which proved that the PCV was electropolymerized on the modified electrode.

Figure 3 displayed typical morphologies of pure MWCNTs (a) and poly-PCV/MWCNTs/GCE (b) characterized by SEM. From Figure 3(a), it can be seen that the MWCNTs were in small bundles and distributed homogeneously exhibiting a special three-dimensional structure. Compared with Figure 3(a), after PCV was electropolymerized on the MWCNTs/GCE, the composite structure changed significantly, as shown in Figure 3(b), which had an obvious formation of composite film.

Electrochemical properties of the poly-PCV/MWCNTs/GCE

The activity of PCV was one of the important factors that work on the electrocatalytic current for the

H₂O₂ sensor. The buffer solution's pH value affected the activity of PCV, and the redox response of the poly-PCV film would be pH dependent. Therefore, voltammetric responses of the poly-PCV/MWCNTs-modified GCE were studied in buffer solution with pH values varying from 4.0 to 8.0. As shown in Figure 4, the peak currents of voltammograms increased with the pH value and showed a maximum value when pH was about 6.0, and then the peak currents began to decrease with increasing pH value. Therefore, pH 6.0 was selected as the optimum pH value in the following experiments.

It could be seen from Figure 4 (inset) that the pH dependence of oxidation peak potentials of PCV obeys the equations, $E_p(V) = 0.4834 - 0.0585 \text{ pH}$ ($R^2 = 0.9966$). The slope of 58.5 mV/pH was closed to the theoretical value of Nernst response, suggesting that equal numbers of electrons and protons take part in the electrode reaction. When the potential was scanned between +0.4 and -0.2 V, one double reversible redox waves were observed attributed to the reduction and oxidation of quinine-

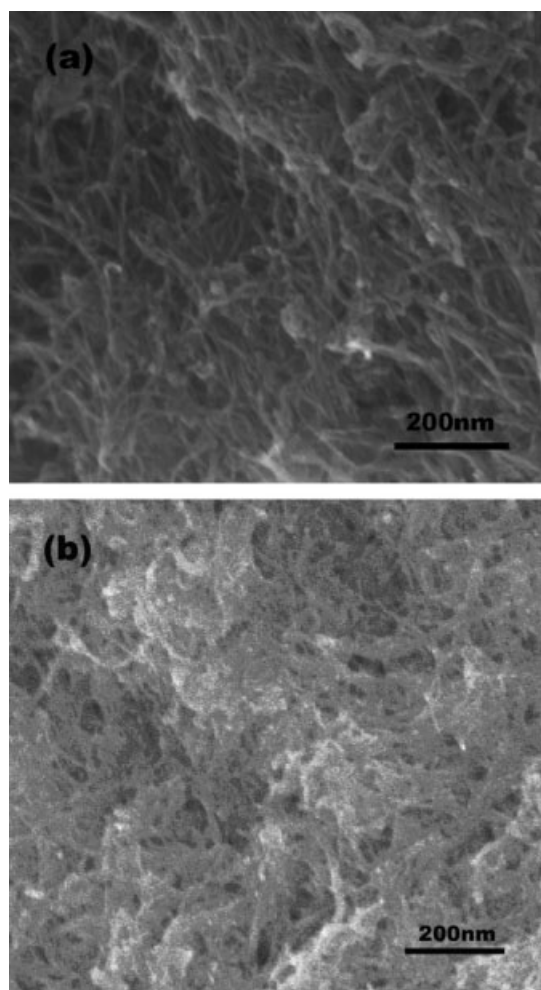


Figure 3 The SEM images of (a) pure MWCNTs and (b) poly-PCV/MWCNTs modified GCE.

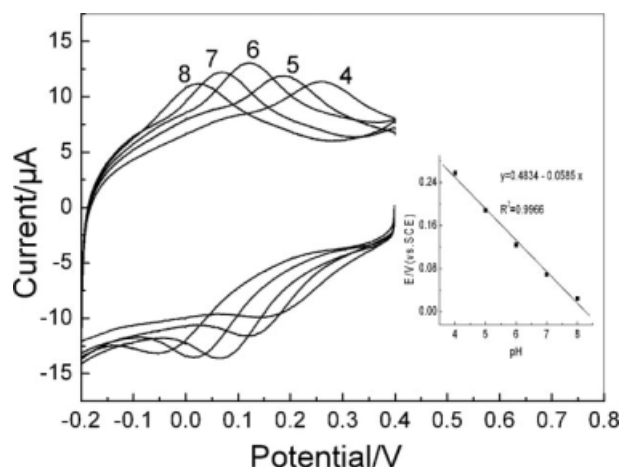
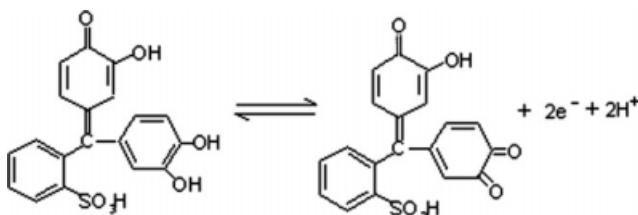


Figure 4 CVs of the poly-PCV/MWCNTs/GCE in 0.1M PBS at various pH values: (a) 4.0; (b) 5.0; (c) 6.0; (d) 7.0; and (e) 8.0. Scan rate: 50 mV/s. Inset: plot of E versus pH value.

hydroquinone functionalities. The possible redox process of poly-PCV on the MWCNTs-modified electrode was shown as follows³⁸:



The dependence of redox peaks of the poly-PCV/MWCNTs/GCE on the scan rates was investigated as shown in Figure 5. The peak currents of cathodic

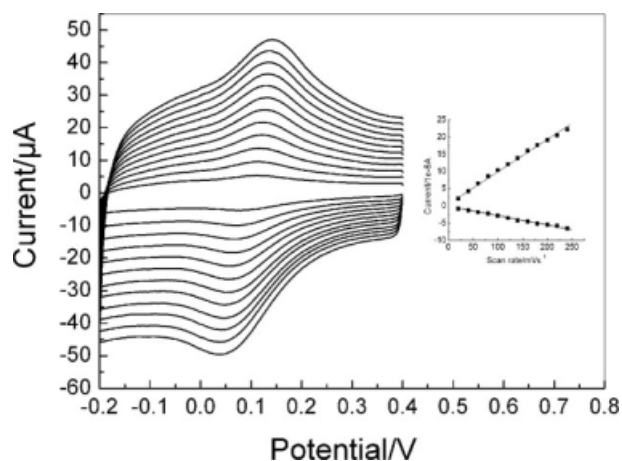


Figure 5 CVs of the poly-PCV/MWCNTs/GCE in 0.1M PBS (pH 6.0) at various scan rates (from inner to outer curve): 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, and 240 mV/s. Inset graph: plots of peak currents versus scan rate.

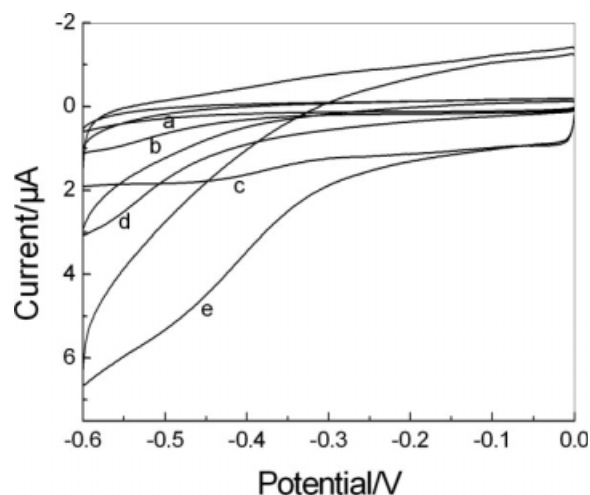


Figure 6 CVs of poly-PCV/MWCNTs/GCE in 0.1M PBS (pH 6.0) in the absence (c) and presence (e) of 10.0 mM H₂O₂, (b,d) as (c,e) for MWCNTs/GCE under the same condition, and (a) for bare GCE with 10.0 mM H₂O₂. Scan rate: 100 mV/s.

and anodic increased linearly with the increase of scan rate, and the peak current (I_p) was proportional to the scan rate (v) from 20 to 240 mV/s (inset, Fig. 5), which indicated a surface-confined wave.

Electrocatalytic reduction of H₂O₂

To address the analytical applicability of poly-PCV/MWCNTs/GCE, electrocatalytic activity of the modified electrode toward the reduction of H₂O₂ was performed with 0.1 PBS (pH 6.0). Figure 6 shows CVs of poly-PCV/MWCNTs/GCE in 0.1M PBS (pH 6.0) in the absence (c) and presence (e) of 10.0 mM H₂O₂, (b and d) as (c and e) for MWCNTs/GCE under the same condition. (a) For bare GCE with 10.0 mM H₂O₂, no obvious current was observed for H₂O₂ reduction at the bare GCE over the potential range 0 to -0.6 V. However, with the MWCNTs-modified GCE (d), a small cathodic current was observed for the reduction of H₂O₂. In contrast, at the poly-PCV/MWCNTs-modified GCE (e), a higher cathodic current appears at more positive potential for the reduction of H₂O₂. These results indicated that the poly-PCV/MWCNTs/GCE showed lower overpotential for H₂O₂ than PCV modified CCE³⁸ and possessed the relatively remarkable catalytic ability to H₂O₂ reduction. The results of experiment also demonstrated the poly-PCV could act as a promoter to enhance the electrochemical reaction and to increase the rate of electron transfer, and the obvious catalytic current could result from the poly-PCV/MWCNTs composite film on the electrocatalytic reduction of H₂O₂.

Chronoamperometric response to H₂O₂ and calibration curve

The poly-PCV/MWCNTs/GCE displayed to be excellent amperometric sensors for H₂O₂. Based on the CV results described earlier, the modified electrode facilitated low-potential amperometric detection of H₂O₂, and amperometric current-time response was recorded to estimate the detection limit and the calibration curve for H₂O₂ detection at the poly-PCV/MWCNTs/GCE. The typical steady-state catalytic current-time curve of the sensor in PBS (pH 6.0) at an applied potential -0.4 V (versus SCE) is shown in Figure 7. The electrochemical response to H₂O₂ displayed a linear range from $2.0 \mu\text{M}$ to 2.4 mM , and the detection limit was estimated to be $0.7 \mu\text{M}$ based on the criterion of signal-to-noise ratio of 3 ($S/N = 3$), which was lower than that of $4 \mu\text{M}$ at PCV-modified CCE.³⁸ The selectivity of the sensor was evaluated, and electroactive substances such as ascorbic acid and uric acid had no obvious interference on the detection of H₂O₂.

The linear range and detection limit of various electroanalytic methods proposed for determination of H₂O₂ were compared with our analytical data in Table I. From the data shown, a lower limit of detection and wide linear range for the detection of H₂O₂ could be achieved using the proposed methods. Our results were good when comparable with exciting methods, and this new biosensor could be useful in the electroanalysis of H₂O₂.

Reproducibility and stability

The reproducibility and stability of the developed biosensor were explored. The reproducibility of modified electrodes, which were independently con-

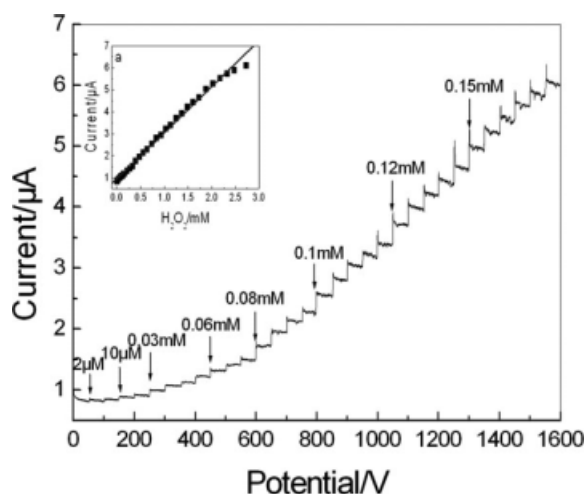


Figure 7 Typical steady-state response of the sensor to successive injection of H₂O₂ into the stirring 0.1M PBS (pH 6.0). The inset was the calibration curve. Applied potential: -0.4 V.

TABLE I
Comparison of Modified Electrodes for Determination of H₂O₂

Modified electrode	Linear range (μM)	Detection limit (μM)	References
TH/MWCNTs/Nf/PIGE	1.37–344	–	30
HRP/Ugi-4CR/AuE	70–8800	0.3	40
PB bluk/GCE	1.2–100	0.4	42
Ag-DNA/GCE	2.0–2500	0.6	45
PCV/CCE	7.8–160	4	38
Poly-PCV/MWCNTs/GCE	2.0–2400	0.7	This work

structed, based on the same bare electrode was 5% (RSD, $n = 8$). The stability was investigated by CV in 0.1M PBS (pH 6.0). The results showed that the poly-PCV/MWCNTs/GCE exhibited one well-defined pair of redox peaks after scanning from $+0.4$ to -0.2 V. After 100 continuous cycles with a scan rate of 100 mV/s , the peak current of the cyclic voltammogram decreased less than 6% and the peak potential almost unchanged. The high stability of the MWCNTs-based H₂O₂ sensor may originate from the advantage of MWCNTs and poly-PCV comodifier.

CONCLUSION

In this work, a novel H₂O₂ sensor based on electropolymerizing PCV on MWCNTs-modified GCE was fabricated. This is the first application of poly-PCV/MWCNTs film to prepare an electrochemical H₂O₂ biosensor with a favorable performance for the rapid detection of H₂O₂. Our experiments confirmed that the sensor showed the satisfied electrocatalytic ability for the reduction of H₂O₂. The high selectivity, low cost, fast amperometric response, a low detection limit, and a wide linear range are the main features of the proposed sensor. Compared with previous H₂O₂ sensors with MWCNTs or PCV film, this poly-PCV/MWCNTs/GCE with its large surface area and good charge-transport characteristics improved detection sensitivity for H₂O₂ reduction.

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